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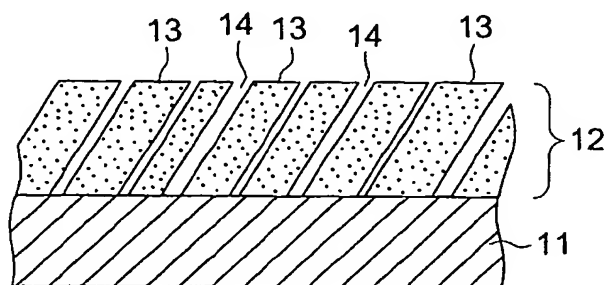
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**(54) Radiation image conversion panel and preparation method thereof**

(57) A radiation image conversion panel is disclosed, comprising on a support a stimutable phosphor layer comprising a stimutable phosphor, wherein the

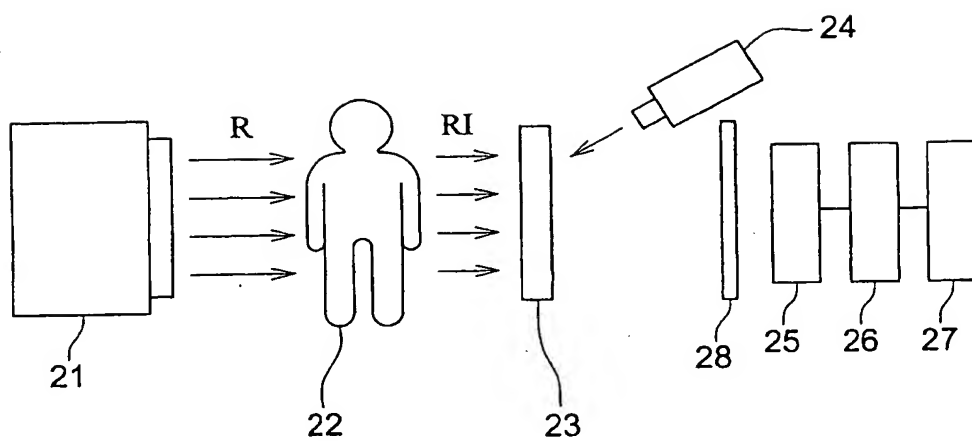
stimulable phosphor layer is formed by vapor deposition on the support which is comprised of a polymer material. A preparation method thereof is also disclosed.

**FIG. 1**



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FIG. 3



## Description

## FIELD OF THE INVENTION

5 [0001] The present invention relates to a radiation image conversion panel and a method for preparing the same (hereinafter, also denoted simply as a preparation method).

## BACKGROUND OF THE INVENTION

10 [0002] Although so-called radiography employing silver halide photography is conventionally used to obtain radiographic images, there also has been developed a radiographic imaging method not using silver halide photographic material. Thus, an imaging method is disclosed, in which radiation that has been transmitted through an object is absorbed by phosphor, followed by exciting the phosphor with energy to cause the radiation energy accumulated in the phosphor to radiate in the form of fluorescence, and imaging is achieved by detecting the fluorescence.

15 [0003] Specifically, U.S. Patent No. 3,859,527 discloses a radiation image conversion method, in which a panel comprising on a support a photostimulable phosphor layer is employed using either or both visible light and infrared rays as the stimulating energy. There have been developed radiation image conversion methods using a photostimulable phosphor (hereinafter, also denoted simply as a stimutable phosphor) exhibiting enhanced luminance and high sensitivity, including, for example, a radiation image conversion method employing BaFX:Eu<sup>2+</sup> type phosphor (X:Cl, Br, I), as described in JP-A No. 59-75200 (hereinafter, the term, JP-A refers to Japanese Patent Application Publication); a radiation image conversion method employing an alkali halide phosphor, as described in JP-A No. 61-72087; a radiation image conversion method employing an alkali halide phosphor containing, as co-activators, Tl<sup>+</sup> and metals such as Ce<sup>3+</sup>, Sm<sup>3+</sup>, Eu<sup>3+</sup>, Y<sup>3+</sup>, Ag<sup>+</sup>, Mg<sup>2+</sup>, Pb<sup>2+</sup> or In<sup>3+</sup>, as described in JP-A Nos. 61-73786 and 61-73787.

25 [0004] Recently, a radiation image conversion panel exhibiting further enhanced sharpness has been desired in the field of diagnostic image analysis. Of these, an attempt in controlling the form of stimutable phosphor grains to enhance sensitivity and sharpness was made as a means for improving sharpness of radiographic images. For example, JP-A No. 61-142497 discloses a method of using a stimutable phosphor layer comprising a fine columnar block which has been formed by sedimentation of a stimutable phosphor on a support having fine protruded patterns; JP-A 62-39737 discloses a method of using a radiation image conversion panel having a stimutable phosphor layer having a pseudo-columnar form which has been formed by producing cracks on the layer surface side; JP-A 62-110200 proposes a method in which a stimutable phosphor layer having voids is formed by vapor deposition onto the upper surface of a support, followed by growing voids by subjecting the surface to a heating treatment to produce cracks.

[0005] JP-A No. 2-58000 proposed a radiation image conversion panel having a stimutable phosphor layer, in which long and thin columnar crystals were formed with an incline at a given angle toward the direction normal to the support.

35 [0006] In the foregoing attempts to control the form of a stimutable phosphor layer, it was intended to enhance image quality by allowing the phosphor layer to have a columnar crystal structure. It was supposed that the columnar form prevented traverse diffusion of stimulated emission light (or photo-stimulated luminescence), i.e., the light reached the support surface with repeating reflection at the interface of cracks (or columnar crystals), thereby leading to markedly enhanced sharpness of images formed by the stimulated luminescence.

40 [0007] Recently, a radiation image conversion panel using a stimutable phosphor containing an alkali halide such as CsBr as a basic substance and Eu as an activator, and the use of activator Eu leading to enhanced X-ray conversion efficiency, which had formerly not been achieved. However, Eu has properties of marked thermal diffusion and the vapor pressure being relatively high under vacuum, resulting in problems such that Eu is easily scattered and localizes in the basic substance. As a result, it becomes difficult to attain enhanced X-ray conversion efficiency by using Eu as an activator and practical use in the market has not yet achieved.

45 [0008] Further, in the technology of using rare earth elements such as Eu as an activator, it was difficult to achieve superior homogeneity of an activator in the formation of a vapor deposit layer under vacuum, only by controlling vapor pressure characteristics, as described in JP-A No. 2002-72381, 2002-20742 and 2002-6092. Specifically when a stimutable phosphor layer was formed by the vapor phase process (or vapor deposition), there were often conducted heating treatments, such as heating raw material, heating a support during vacuum deposition and annealing (for relaxation of substrate strain) after forming the layer, so that the existing state of the activator was varied, causing non-uniform presence of an activator in the layer. However, such heating treatments are indispensable to provide durability to the stimutable phosphor layer.

50 [0009] Accordingly, improvements are desired with respect to luminance, sharpness and homogeneity of the activator contained in the phosphor layer, as required as a radiation image conversion panel on the market.

## SUMMARY OF THE INVENTION

[0010] It is an object of the present invention to provide a radiation image conversion panel exhibiting superior homogeneity of an activator in a stimuable phosphor layer (hereinafter, also denoted simply as a phosphor layer) and enhanced luminance and sharpness, and a preparation method of the same.

[0011] The foregoing object can be accomplished by the following constitution:

1. A radiation image conversion panel comprising on a support at least one stimuable phosphor layer, wherein the stimuable phosphor layer has a thickness of 50  $\mu\text{m}$  to 20 mm and the support is comprised of a polymer material, and the stimuable phosphor layer is formed by a process comprising depositing a stimuable phosphor on the support by vapor deposition.

2. A method of preparing a radiation image conversion panel comprising on a support a stimuable phosphor layer, the method comprising:

depositing a stimuable phosphor on the support by vapor deposition to form the stimuable phosphor layer,

wherein the support is comprised of a polymer material.

## BRIEF EXPLANATION OF THE DRAWING

[0012]

Fig. 1 illustrates a stimuable phosphor layer having columnar crystals formed on the support by a process of vapor deposition (or vapor phase growth).

Fig. 2 illustrates the mode of forming a stimuable phosphor layer on a support by the vapor deposition method.

Fig. 3 shows an example of obtaining a transmission-type radiation image using a radiation image conversion panel according to the invention.

Fig. 4 illustrates formation of a stimuable phosphor layer by vapor deposition.

## DETAILED DESCRIPTION OF THE INVENTION

[0013] One aspect of this invention is directed to a radiation image conversion panel comprising on a support a stimuable phosphor layer. The stimuable phosphor layer is a layer of a layer of vapor-deposited stimuable phosphor, that is, a stimuable phosphor is deposited on the support (or substrate) by the vapor deposition process. The support used in this invention is formed of a polymer material. The use of a polymer material as a support results in the support (or substrate) being uniformly heated and uniformly dissipating the heat during formation of columnar crystals, leading to columnar crystals having a small top diameter and a relatively short height.

[0014] To perform vapor deposition with maintaining tensile strength of the support, the glass transition temperature of the polymer material is preferably 150 to 350  $^{\circ}\text{C}$  in regard to heat resistance.

[0015] In the process of forming the stimuable phosphor layer on the support by vapor deposition so as to have a layer thickness of 50 to 20 mm, the support is arranged preferably in a fan form (roof-form) to perform vapor deposition. Thus, to avoid thermal influence and achieve uniform heat distribution, a dome-form substrate holder is provided so that vapor streams form an outgoing angle of at least  $20^{\circ}$  with respect to the evaporation source, thereby allowing an activator to be homogeneously deposited in the phosphor layer.

[0016] Allowing an activator to be homogeneously deposited in the phosphor layer means that the activator content of the support side of the phosphor layer is substantially the same as that of the surface side of the phosphor layer. Specifically, the activator content of the support side coincides with that of the surface side preferably within  $\pm 10\%$ . For example, a sample obtained by shaving off a ca. 500  $\mu\text{m}$  thick phosphor layer to a depth of 100  $\mu\text{m}$  from the surface side, and that from the support side are each dissolved in water to form an aqueous solution. The respective aqueous solutions are subjected to ICP emission spectrometry to determine the activator content.

[0017] In the radiation image conversion panel according to this invention, the support is preferably comprised of at least two layers, and more preferably three layers. Thus, it is preferred to use a support comprising plural layers to obtain a support exhibiting a relatively low X-ray absorption and having superior flatness, and it is more preferred to form plural layers using a film sheet exhibiting an X-ray absorbance at 80 kVp of less than 10%.

[0018] In this invention, the support is preferably comprised of plural layers containing a carbon fiber plate, which is obtained by laminating thin film sheets achieving a precise plane flatness at the time of deposition together with a rigid carbon fiber plate. As a thin film sheet can be employed plastic material such as polyimide or PET (polyethylene terephthalate) as well as metals such as Cu (copper), Al (aluminum) and stainless steel.

[0019] In one preferred embodiment of this invention, the support comprises polyimide, carbon fiber plate and polyimide in that order, thereby resulting in enhanced advantages of this invention.

[0020] Polyimide film, for example, Mictron Film or Capton Film (available from Toray Co.) can be employed, which is laminated onto a carbon fiber plate and molded to prepare a support in the following manner. Thus, polyimide sheets, which were previously coated with an adhesive layer or bonded with a adhesive sheet are laminated onto the carbon fiber plate. Alternatively, a carbon fiber plate impregnated with epoxy resin or bismaleimide resin is sandwiched between polyimide sheets and then molded using a molding machine at a temperature of 150 to 300 °C and a pressure of  $9.8 \times 10^5$  to  $6.9 \times 10^6$  Pa over a period of 15 min. to 3 hr. The three-layered support of polyimide/carbon resin fiber plate/polyimide used in Examples, described later was prepared according to the latter method.

[0021] As polyimide sheet, a thickness of at least 50  $\mu\text{m}$  is preferred to reduce protrusions on the support surface and a thickness up to 200  $\mu\text{m}$  is preferred in terms of handling. As carbon fiber plate, a thickness of at least 0.1 mm is preferred in terms of rigidity and a thickness up to 5 mm is preferred in X-ray absorption.

[0022] Fig. 4 illustrates vapor deposition on a substrate (polymer material) according to this invention. The roof-form angle, which is angle  $(\theta_1 + \theta_2)$ , as shown in Fig. 5, is preferably 20° to 70°. An angle of less than 20° forms a narrow opening over the evaporation source, lowering vapor deposition efficiency. An angle of more than 70° spreads an opening over the evaporation source, whereby the deposition efficiency is further enhanced but the heat distribution becomes worse, resulting in an non-homogeneous activator in the phosphor layer. Thus, the foregoing angle is preferably  $20^\circ \leq (\theta_1 + \theta_2) \leq 70^\circ$ , provided that  $\theta_1$  and  $\theta_2$  are not zero at the same time.

[0023] As shown in Fig. 4, the substrates 1 are arranged in a fan form (or roof form) toward the evaporation source 2. Specifically, the substrate is not provided right above the evaporation source but the substrates 1 are arranged at symmetrical angles of 20° (as shown in Fig. 5,  $\theta_1 = 20^\circ$  and  $\theta_2 = 20^\circ$ ), thereby forming a phosphor layer homogeneously containing an activator.

[0024] The upper portion of the evaporation source preferably has a mesh or perforated structure.

[0025] Accordingly, vapor deposition in this invention is conducted preferably under the condition at a vacuum pressure of  $1.33$  to  $1.33 \times 10^{-3}$  Pa and a temperature of 20 to 70 °C (more preferably, 35 to 45 °C).

[0026] The support used in the radiation image conversion panel relating to this invention is comprised of a polymer material.

[0027] Specific examples of such polymer material include plastic resins, such as cellulose acetate resin, polyester resin, polyethylene terephthalate resin, polyamide resin, epoxy resin, polyimide resin, triacetate resin, polycarbonate resin and syndiotactic polystyrene resin. These resins may be used alone or in combination.

[0028] In the radiation image conversion panel according to this invention, the support is preferably comprised of at least two layers, and more preferably at least three layers. Thus, it is preferred to use a support comprising plural layers to obtain a support exhibiting a relatively low X-ray absorption and having superior flatness, and it is more preferred to form plural layers using a film sheet exhibiting an X-ray absorbance at 80 kVp of less than 10%.

[0029] In this invention, the support is preferably comprised of plural layers containing a carbon fiber plate, which is obtained by laminating thin film sheets achieving a precise plane flatness at the time of deposition together with a rigid carbon fiber plate. As a thin film sheet can be employed plastic material such as polyimide or PET (polyethylene terephthalate) as well as metals such as Cu (copper), Al (aluminum) and stainless steel.

[0030] In one preferred embodiment of this invention, the support comprises polyimide, carbon fiber plate and polyimide in that order, thereby resulting in enhanced advantages of this invention.

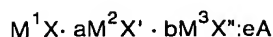
[0031] Polyimide film, for example, Mictron Film or Capton Film (available from Toray Co.) can be employed, which is laminated onto a carbon fiber plate and molded to prepare a support in the following manner. Thus, polyimide sheets, which were previously coated with an adhesive layer or bonded with a adhesive sheet are laminated onto the carbon fiber plate. Alternatively, a carbon fiber plate impregnated with epoxy resin or bismaleimide resin is sandwiched between polyimide sheets and then molded using a molding machine at a temperature of 150 to 300 °C and a pressure of  $9.8 \times 10^5$  to  $6.9 \times 10^6$  Pa over a period of 15 min. to 3 hr. The three-layered support of polyimide/carbon resin fiber plate/polyimide used in Examples, described later was prepared according to the latter method.

[0032] As polyimide sheet, a thickness of at least 50  $\mu\text{m}$  is preferred to reduce protrusions on the support surface and a thickness up to 200  $\mu\text{m}$  is preferred in terms of handling. As carbon fiber plate, a thickness of at least 0.1 mm is preferred in terms of rigidity and a thickness up to 5 mm is preferred in X-ray absorption.

[0033] The support may be smooth-surfaced, or it may be matted in order to enhance adhesion of the support to the stimuable phosphor layer. To enhance adhesion between the support and stimuable phosphor layer, the surface of the support may optionally be provided with an adhesion promoting layer in advance. A thickness of the support, depending on material, is usually 80 to 2000  $\mu\text{m}$ , and preferably 80 to 1000  $\mu\text{m}$  in terms of handling.

[0034] The stimuable phosphor used in this invention preferably is one represented by the following formula (1):

formula (1)



wherein  $M^1$  is at least one alkali metal atom selected from the group consisting of Li, Na, K, Rb and Cs;  $M^2$  is at least one divalent metal atom selected from the group consisting of Be, Mg, Ca, Sr, Ba, Zn, Cd, Cu and Ni;  $M^3$  is at least one trivalent metal atom selected from the group consisting of Sc, Y, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Al, Ga and In; X, X' and X'' are each a halogen atom selected from the group consisting of F, Cl, Br and I; A is a metal atom selected from the group consisting of Eu, Tb, In, Ce, Tm, Dy, Pr, Ho, Nd, Yb, Er, Gd, Lu, Sm, Y, Ti, Na, Ag, Cu and Mg; a, b and e are each

$0 \leq a < 0.5$ ,  $0 \leq b < 0.5$  and  $0 < e \leq 0.2$ .

[0035] In the formula (1),  $M^1$  is at least one alkali metal atom selected from the group consisting of Li, Na, K, Rb and Cs, preferably at least one alkali metal atom selected from Rb and Cs atoms, and more preferably Cs atom.

[0036]  $M^2$  represents a divalent metal selected from the group consisting of Be, Mg, Ca, Sr, Ba, Zn, Cd, Cu and Ni. Of these, a divalent metal selected from the group consisting of Be, Mg, Ca, Sr, and Ba is preferred.

[0037]  $M^3$  represents a trivalent metal selected from the group consisting of Sc, Y, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Al, Ga. Of these, a trivalent metal selected from the group consisting of Y, Ce, Sm, Eu, Al, Gd, Lu, Ga and In is preferred.

[0038] A represents a metal selected from the group consisting of Eu, Tb, In, Ce, Tm, Dy, Pr, Ho, Nd, Yb, Er, Gd, Lu, Sm, Y, Ti, Na, Ag, Cu and Mg.

[0039] X, X' and X'' are each at least one halogen atom selected from the group consisting of F, Cl, Br and I, preferably at least one halogen atom selected from F, Cl and Br, and more preferably Br in terms of enhancing stimulated emission of a stimuable phosphor.

[0040] The foregoing stimuable phosphor preferably is one represented by the following formula (2):

formula (2)



wherein  $M^1$ , X, A and e are each the same as defined in the foregoing formula (1).

[0041] In the formula (1), "a" is  $0 \leq a < 0.5$  and preferably  $0 \leq a < 0.01$ ; "b" is  $0 \leq b < 0.5$ , and preferably  $0 \leq b \leq 0.01$ ; "e" is  $0 < e \leq 0.2$ , and preferably  $0 < e \leq 0.1$ .

[0042] The stimuable phosphor represented by formula (1) can be prepared, for example, in the following manner.

[0043] First, an acid (HI, HBr, HCl or HF) is added to a carbonate so as to form a composition of a phosphor raw material described below and after mixed with stirring, the mixture is filtered at a point of neutralization, and the filtrate was evaporated to obtain crystals having the following composition.

[0044] As phosphor raw material, at least one compound selected from each of the following groups (a) and (b), and a compound containing a metal atom selected from the following group (c) are used:

(a) NaF, NaCl, NaBr, NaI, KF, KCl, KBr, KI, RbF, RbCl, RbBr, RbI, CsF, CsCl, CsBr, and CsI;

(b)  $MgF_2$ ,  $MgCl_2$ ,  $MgBr_2$ ,  $MgI_2$ ,  $CaF_2$ ,  $CaCl_2$ ,  $CaBr_2$ ,  $CaI_2$ ,  $SrF_2$ ,  $SrCl_2$ ,  $SrBr_2$ ,  $SrI_2$ ,  $BaF_2$ ,  $BaCl_2$ ,  $BaBr_2$ ,  $BaI_2$ ,  $ZnF_2$ ,  $ZnCl_2$ ,  $ZnBr_2$ ,  $ZnI_2$ ,  $CdF_2$ ,  $CdCl_2$ ,  $CdBr_2$ ,  $CdI_2$ ,  $CuF_2$ ,  $CuCl_2$ ,  $CuBr_2$ ,  $CuI_2$ ,  $NiF_2$ ,  $NiCl_2$ ,  $NiBr_2$  and  $NiI_2$ ;

(c) Eu, Tb, In, Cs, Ce, Tm, Dy, Pr, Ho, Nd, Yb, Er, Gd, Lu, Sm, Y, Ti, Na, Ag, Cu and Mg.

[0045] As activator raw material, a compound containing a metal atom selected from the following group (d) is used:

(d) Eu, Tb, In, Cs, Ce, Tm, Dy, Pr, Ho, Nd, Yb, Er, Gd, Lu, Sm, Y, Ti, Na, Ag, Cu and Mg.

[0046] Phosphor raw materials, which have been selected from the foregoing (a) to (d) so as to have mixing composition meeting the numerical range, as defined in this invention are weighed and dissolved in pure water. In this regard, there may be conducted sufficient mixing using a mortar, ball mill or mixer mill. Then, a prescribed amount of an acid is added to adjust a pH value (C) of the thus obtained solution so as to fall within the range of  $0 < C < 7$ , and then any water is vaporized.

[0047] Further, the obtained raw material mixture is charged into a heat-resistant vessel such as a silica port, an alumina crucible or a silica crucible and then placed in an electric furnace to be calcined. The calcination temperature preferably is 500 to 1000 °C. The calcination time, depending on a charging amount of raw materials, calcination temperature and the like, preferably is 0.5 to 6 hrs. As a calcinations atmosphere is employed a weakly reducible

atmosphere such as a nitrogen gas atmosphere containing a small amount of hydrogen gas or a carbon dioxide atmosphere containing carbon monoxide, a nitrogen gas atmosphere, a neutral atmosphere such as an argon gas atmosphere, or a trace amount of oxygen-introduced weakly oxidizing atmosphere.

**[0048]** After completion of calcination under the foregoing condition, calcined material is taken out of the electric furnace and subjected to pulverization. Thereafter, powdery calcined material may again be charged into a heat resistant vessel and then placed in an electric furnace to be calcined under the foregoing condition to further enhance emission luminance of the phosphor. When the calcined material is allowed to cool from calcination temperature to room temperature, the intended phosphor can be obtained by being taken out the calcined material from an electric furnace and allowing it to stand in an aerial atmosphere. In this regard, the calcined material may be cooled in the same atmosphere as in the calcination, such as a weakly reducing atmosphere or neutral atmosphere. Alternatively, the calcined material is moved from a heating section to a cooling section within the electric furnace, followed by being rapidly cooled in a weakly reducing atmosphere, neutral atmosphere or weakly oxidizing atmosphere, thereby leading to further enhanced stimulated emission luminance of the phosphor.

**[0049]** The stimutable phosphor layer relating to this invention is a layer of vapor deposited stimutable phosphor and is formed by vapor deposition (or vapor-phase deposition process). The phosphor layer being formed by a process of vapor deposition means that the phosphor layer is formed by a process comprising depositing a stimutable phosphor on the support in the vapor phase to form the stimutable phosphor layer. Thus, the stimutable phosphor is deposited on the support in the vapor phase deposition process to form the phosphor layer (preferably having a thickness of 50  $\mu\text{m}$  to 20 mm).

**[0050]** A vacuum evaporation method, a sputter deposition method, a CVD (chemical vapor deposition) method, ion plating method and other methods have been employed to deposit the stimutable phosphor on the support to form a stimutable phosphor layer.

**[0051]** The foregoing methods are conducted, for example, in the manner described below.

**[0052]** Vacuum evaporation is conducted in such a manner that after placing a support in an evaporation apparatus, the inside of the apparatus is evacuated to a vacuum degree of  $1.333 \times 10^{-4}$  Pa and subsequently, at least a stimutable phosphor is evaporated with heating by the resistance heating method or electron-beam method to cause the phosphor to be deposited at a slant on the surface of the support to a desired thickness. As a result, a stimutable phosphor layer containing no binder is formed, provided that the foregoing evaporation stage may be divided into plural times to form the stimutable phosphor layer. In this evaporation stage, plural resistance heaters or electron beams may be used to perform vacuum evaporation. Alternatively, raw material of a stimutable phosphor is evaporated using plural resistance heaters or electron beams and the intended stimutable phosphor is synthesized on the support, simultaneously forming a stimutable phosphor layer. After completion of vapor evaporation, a radiation image conversion panel of this invention can be prepared by optionally providing a protective layer on the opposite side of the stimutable phosphor layer to the support. Vacuum evaporation may be conducted while cooling or heating the substrate to be deposited thereon. After completion of vacuum evaporation, the stimutable phosphor layer may be subjected to a heating treatment. In vapor evaporation, a gas such as  $\text{O}_2$  or  $\text{H}_2$  may optionally be introduced to perform reactive vapor evaporation.

**[0053]** Sputter deposition is conducted in such a manner that after setting a support in a sputtering apparatus, the inside of the apparatus is evacuated to a vacuum level of  $1.333 \times 10^{-4}$  Pa and then inert gas used for sputtering such as Ar and Ne is introduced therein at a gas pressure of ca.  $1.333 \times 10^{-1}$  Pa, subsequently, sputtering is carried out with targetting the stimutable phosphor to cause the phosphor to be deposited on the slanted surface of the support so as to have a desired thickness. Similarly to the vacuum evaporation, various treatments may be applied.

**[0054]** Further, there are also applicable the CVD method and ion plating method.

**[0055]** The growth rate of a stimutable phosphor layer in the vapor deposition preferably is 0.05 to 300  $\mu\text{m}/\text{min}$ . A growth rate of less than 0.05  $\mu\text{m}/\text{min}$  results in lowered productivity of the radiation image conversion panel of this invention and is not preferable. In the case of a growth rate of more than 300  $\mu\text{m}/\text{min}$ , it is difficult to control the growth rate and is not unsuitable.

**[0056]** A radiation image conversion panel which has been prepared by the vapor evaporation method or sputter deposition method contains no binder, leading to increased filling density of the stimutable phosphor layer and thereby a radiation image conversion panel with enhanced sensitivity and sharpness can be obtained.

**[0057]** A thickness of the stimutable phosphor layer, depending on the intended use of the radiation image conversion panel and the kind of stimutable phosphor, preferably is 50  $\mu\text{m}$  to 1mm, more preferably 50 to 300  $\mu\text{m}$ , still more preferably 100 to 300  $\mu\text{m}$ , and optimally 150 to 300  $\mu\text{m}$ .

**[0058]** In the formation of a stimutable phosphor layer by the vapor deposition, a support on which the stimutable phosphor layer is to be formed, is preferably heated at a temperature of 100  $^{\circ}\text{C}$  or higher, more preferably 150  $^{\circ}\text{C}$  or higher, and still more preferably 150 to 400  $^{\circ}\text{C}$ .

**[0059]** The reflectance of a stimutable phosphor layer preferably is not less than 20%, more preferably not less than 30%, and still more preferably not less than 40%, with an upper limit of 100%.

**[0060]** Further, spacing between columnar crystals may be filled with a filler such as a binder to strengthen the

phosphor layer. Furthermore, material exhibiting relatively high light absorbance or high reflectance may be used as filler. The use thereof prevents lateral diffusion of stimulating light entering the phosphor layer, in addition to the foregoing strengthening effect.

[0061] Next, formation of the stimuable phosphor of this invention will be described based on Figs. 1 and 2. Fig. 1 exemplarily illustrates a stimuable phosphor layer having columnar crystals formed on the support. In the Fig. 1, the numeral 11 designates a support, the numeral 12, a stimuable phosphor layer, and numeral 13, columnar crystals forming the stimuable phosphor layer. The numeral 14 indicates spacing between columnar crystals.

[0062] Fig. 2 illustrates the mode of forming a stimuable phosphor layer on a support by the vacuum evaporation method, in which vapor streams (16) of a stimuable phosphor are introduced at an incident angle  $\theta_2$  (in the Figure, 60°) to the line (R) normal to the support surface to form columnar crystals on the support, at an angle of  $\theta_1$  (in the Figure, 30°, empirically, about a half of the incident angle).

[0063] The stimuable phosphor layer formed on the support contains no binder, leading to superior directionality and enhanced directionality of stimulating light and stimulated luminescence and enabling formation of a thicker phosphor layer, as compared to radiation image conversion panel having a dispersion-type stimuable phosphor layer, in which a stimuable phosphor is dispersed in a binder. Moreover, reduced scattering of stimulating light in the stimuable phosphor layer results in enhanced sharpness.

[0064] Further, spacing between columnar crystals may be filled with a filler such as a binder to strengthen the phosphor layer. Furthermore, material exhibiting relatively high light absorbance or high reflectance may be used as filler. The use thereof prevents lateral diffusion of stimulating light entering the phosphor layer, in addition to the foregoing strengthening effect. Material exhibiting high reflectance refers to one exhibiting a high reflectance with respect to stimulating light (500 to 900 nm, specifically 600 to 800 nm), including metals such as aluminum, magnesium, silver and indium, white pigments and colorants ranging green to red.

[0065] White pigments can also reflect stimulating light. Examples thereof include  $\text{TiO}_2$  (anatase type, rutile type),  $\text{MgO}$ ,  $\text{PbCO}_3$ ,  $\text{Pb(OH)}_2$ ,  $\text{BaSO}_4$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{M(II)FX}$  [in which  $\text{M(II)}$  is at least one of Ba, Sr and Ca, X is at least one of Cl and Br],  $\text{CaCO}_3$ ,  $\text{ZnO}$ ,  $\text{Sb}_2\text{O}_3$ ,  $\text{SiO}_2$ ,  $\text{ZrO}_2$ , lithopone ( $\text{BaSO}_4 \cdot \text{ZnS}$ ), magnesium silicate, basic lead silisulfate, and aluminum silicate. These white pigments exhibit high covering power and have a refractive index high, whereby stimulated luminescence is easily scattered through reflection or refraction, leading to enhanced sensitivity of the radiation image conversion panel.

[0066] Examples of material exhibiting high light absorbance include carbon, chromium oxide, nickel oxide, iron oxide, and blue colorants. Of these, carbon absorbs stimulated luminescence.

[0067] Colorants may be any organic or inorganic colorants. Examples of organic colorants include Zapon Fastblue 3G (produced by Hoechst A.G.), Estrol Brillblue N-3RL (produced by Sumitomo Chemical Ind. Co.Ltd.), D6CBlue No. 1 (produced by National Aniline Co.), Spirit Blue (produced by HODOGAYA KAGAKU Co., Ltd.), Oilblue No. 603 (produced by Orient Co., Ltd.), Kiton Blue A (produced by Chiba Geigy Co.), Aisen Catironblue GLH (produced by HODOGAYA KAGAKU Co., Ltd.), Lakeblue AFH (produced by KYOWA SANGYO Co., Ltd.), Primocyanine 6GX (produced by INAHATA SANGYO Co., Ltd.), Brillacid Green 6BH (produced by HODOGAYA KAGAKU Co., Ltd.), Cyanblue BNRCS (produced by Toyo Ink Co., Ltd.), and Lyonoyl Blue SL (produced by Toyo Ink Co., Ltd.). There are also cited organic metal complex colorants such as Color Index 24411, 23160, 74180, 74200, 22800, 23154, 23155, 24401, 14830, 15050, 15760, 15707, 17941, 74220, 13425, 13361, 13420, 11836, 74140, 74380, 74350 and 74460. Examples of inorganic colorants include ultramarine, cobalt blue, celureun blue, chromium oxide, and  $\text{TiO}_2\text{-ZnO-NiO}$  type pigments.

[0068] The stimuable phosphor layer may be provided thereon with a protective layer. The protective layer may be formed by coating a coating composition for the protective layer on the stimuable phosphor layer or the protective layer which was previously prepared may be adhered to the support. Alternatively, a procedure of forming a stimuable phosphor layer on the protective layer which was previously prepared is also applicable. Materials used for the protective layer include those which are usually used for protective layers. Examples thereof include cellulose acetate, nitrocellulose, polymethyl methacrylate, polyvinyl butyral, polyvinyl formal, polycarbonate, polyester, polyethylene terephthalate, polyethylene, polyvinylidene chloride, nylon, polytetrafluoroethylene, polytrifluoroethylene, copolymer of tetrafluoroethylene and hexafluoropropylene, copolymer of vinylidene chloride and vinyl chloride, and copolymer of vinylidene chloride and acrylonitrile. Further, a transparent glass substrate may be used as a support. Furthermore, inorganic material such as  $\text{SiC}$ ,  $\text{SiO}_2$ ,  $\text{SiN}$ , and  $\text{Al}_2\text{O}_3$  may be allowed to deposit by means of the vacuum evaporation or sputtering method to form the protective layer. The thickness of a protective layer is preferably 0.1 to 2,000  $\mu\text{m}$ .

[0069] Fig. 3 illustrates a constitution of a radiation image conversion panel of this invention. In Fig. 3, the numeral 21 designates a radiation generating apparatus, 22 designates an object, 23 designates a radiation image conversion panel having a visible- or infrared-stimuable phosphor layer, 24 designates a stimulating light source to cause a latent image stored in the radiation image conversion panel (23) to be emitted as stimulated luminescence, 25 designates a photoelectric conversion apparatus to detect the stimulated luminescence emitted from the radiation image conversion panel (23), 26 designates an image reproduction apparatus to reproduce photoelectric conversion signals detected in the photoelectric conversion apparatus (25) in the form of an image, 27 designates a display apparatus to display



reproduced images, and 28 designates a filter for reflected light from a light source (24) to allow only light emitted from the radiation image conversion panel (23) to pass therethrough. Fig. 3 shows an example of obtaining a transmission-type radiation image, and in cases where the object (22) itself radiates radiation, a radiation generation apparatus (21) may not be required. An apparatus subsequent to the photoelectric conversion (25) apparatus may be any one that is

5 capable of reproducing light information from the radiation image conversion panel (23), in any image form.  
**[0070]** As shown in Fig. 3, when the object (22) is arranged between the radiation generation apparatus (21) and the radiation image conversion panel (23), and exposed to radiation (R), the radiation (R) transmits the respective portions of the object (22) in accordance with radiation transmittance thereof and the resulting transmission image (RI), i.e., an image having different radiation intensities enters the radiation image conversion panel (23). The thus entered  
 10 transmission image (RI) is absorbed in a stimuable phosphor layer of the radiation image conversion panel (23), in which electrons and/or holes are generated in proportion to the dose of the absorbed radiation and accumulated at a trap level of the stimuable phosphor to form a latent image accumulating energies of the radiation transmission image. Subsequently, the latent image is excited with light energy to form an actual image, i.e., the stimulated phosphor layer is irradiated with the light source (24) irradiating visible or infrared light to eject the electrons and/or holes accumulated  
 15 on the trap level to emit the accumulated energy in the form of stimulated luminescence. The intensity of the emitted luminescence is proportional to the number of accumulated electrons and/or holes, that is, energy of the radiation absorbed in the stimuable phosphor of the radiation image conversion panel (23). The thus obtained light signals are converted to electric signals by the photoelectric conversion (25) apparatus such as a photomultiplier, which are reproduced as an image in image processor (26), displaying the image in image display apparatus (27). As the image processor (26), it is effective to employ one which not only reproduces the electric signals as the image signal but one which can also conduct image processing, computation, memory and storage of the image.

**[0071]** The stimulated luminescence emitted from the stimuable phosphor layer, having a spectral distribution in the lower wavelength region is preferable, based on the reason that the stimulated luminescence emitted from the stimuable phosphor layer is required to be separated from the reflected stimulating light and photoelectric converters to  
 25 receive the luminescence emitted from the stimuable phosphor layer, in general, are provided with a sensor having higher sensitivity to light energy of 600 nm or less. Emission of stimuable phosphors relating to the invention falls within the wavelength region of 300 to 500 nm and the stimulating light wavelength is 500 to 900 nm, satisfying the foregoing conditions. Further, along with a recent trend of downsizing diagnostic apparatuses, semiconductor lasers which exhibit a higher output and are capable of being further down-sized are preferably employed for use in reading  
 30 images of the radiation image conversion panel. The semiconductor laser has a wavelength of 680 nm and the stimuable phosphor used in the radiation image conversion panel of the invention exhibits extremely superior sharpness when using a stimulating light of 680 nm. Thus, the stimuable phosphors relating to the invention emit luminescence having a main peak at 500 nm or less, which is easily separable from the stimulating light and compatible with spectral sensitivity of the receiver, leading to enhanced light-receiving efficiency and enhanced sensitivity of an image receiving  
 35 system.

**[0072]** Light sources including the stimulating wavelength for the stimuable phosphor used in the radiation image conversion panel (23) are used as the stimulating light source (24). Specifically, the use of laser light simplifies an optical system and leads to enhanced stimulating light intensity, resulting in preferable performance. Examples of the laser include an He-Ne laser, He-Cd laser, Ar ion laser, Kr laser, N<sub>2</sub> laser, YAG laser and its second harmonic wave,  
 40 ruby laser, semiconductor laser, various dye lasers, and metal vapor lasers such as a copper vapor laser. Of these, continuous oscillation lasers such as a He-Ne laser and an Ar ion laser are usually desirable, and pulse-oscillated lasers are also usable by synchronizing the pulse with a scanning time for one pixel of the panel. In cases when employing retarded emission for separation, instead of using the filter (28), the use of the pulse-oscillated laser is preferable rather than modulation of the continuous oscillation laser, as described in JP-A No. 59-22046. Of the various  
 45 laser light sources described above, semiconductor lasers are specifically preferred in terms of being compact, inexpensive and not requiring a modulator.

**[0073]** The filter (28) cuts reflected stimulating light and allows the stimulated luminescence emitted from the radiation image conversion panel (23) to transmit, which is determined by the combination of the stimulated emission wavelength of a stimuable phosphor contained in the radiation image conversion panel (23) and the stimulating light source (24).  
 50 In the preferred practical combination of a stimulating light wavelength of 500 to 900 nm with a stimulated emission wavelength of 300 to 500 nm, for example, violet to blue glass filters are used, such as C-39, C-40, V-40, V-42 and V-44 (available from TOSHIBA CORP.), 7-54 and 7-59 (available from Corning Co.), BG-1, BG-3, BG-25, BG-37 and BG-38 (available from Spectrofilm Co.). Interference filters are usable by selecting specific filters. The photoelectric conversion apparatus (25) usable in the invention includes any one capable of converting variation of luminous energy  
 55 to electric signal, such as a photoelectric tube, a photomultiplier, a photodiode, a phototransistor, a solar cell, and photoconductive elements.

## EXAMPLES

[0074] The present invention will be further described based on examples but embodiments of the invention are by no means limited to these examples.

## Example 1

## Preparation of Radiation Image Conversion Panel

[0075] On the surface of a 200  $\mu\text{m}$  thick crystallized glass support (produced by Nippon Denki Glass Co., Ltd.) was formed a stimuable phosphor layer containing stimuable phosphor (CsBr:Eu) according to the condition shown in Table 1, using a vacuum evaporation apparatus as shown in Fig. 4.

[0076] In the vacuum evaporation, the support was set in the evaporation chamber of an evaporator and then, phosphor raw material, as an evaporation source (CsBr:Eu) which was previously molded in a press was put into a water-cooled crucible. Thereafter, the inside of the evaporator was evacuated and after introducing  $\text{N}_2$  gas to adjust a degree of vacuum of 0.133 Pa, vacuum evaporation was conducted to perform vapor deposition, while maintaining the support temperature (also called substrate temperature) at 350° C. The vapor deposition was completed when the stimuable phosphor layer reached 300  $\mu\text{m}$  thick and then, the phosphor layer was subjected to a heating treatment at 400° C. Peripheral portions of the support and a protective layer comprised of borosilicate glass were sealed with an adhesive in a dry aerial atmosphere to prepare a radiation image conversion panel sample No. 1, comprising tight-shielded a phosphor layer.

[0077] Radiation image conversion panel samples No. 2 through 6 were prepared similarly to sample No. 1, provided that glass support (or substrate) was replaced by 200  $\mu\text{m}$  thick support of polymer materials comprising a polyimide resin (Kapton, produced by Toray Co.) and an epoxy resin (produced by Nippon Ciba Geigy Co.), differing in compounding ratio and glass transition temperature ( $T_g$ ) and an roof-form angle (i.e., angle =  $\theta_1 + \theta_2$ , as shown in Fig.4) was varied, as shown in Table 1.

[0078] Sample No. 7 was prepared similarly to sample No. 4, provided that the support was replaced by the three-layered support prepared as below. Thus, 2 mm thick carbon fiber plate (CFRP plate, available from Toray Co.) was sandwiched between polyimide sheets and molded at a pressure of 20  $\text{kg}/\text{cm}^2$  and a temperature of 200 °C for 15 min. Thereafter, cooling was gradually conducted until reached 100 °C and a three-layered support was obtained.

[0079] Sample No. 8 was prepared similarly to sample No. 4, provided that the support was replaced by the two-layered support prepared as below. An optimum amount of polyvinyl alcohol (M.W., 20,000) was put on a polyimide sheet and further thereon, the carbon fiber plate (CFRP plate, available from Toray Co.) was laminated at a temperature of 150 °C to obtain a two-layered support.

[0080] The carbon fiber plate (2 mm thick) described above exhibited a glass transition temperature of 180 °C and the polyimide sheet (Mictron film, available from Toray-Du Pont) being 100 thick and exhibiting a glass transition temperature of 280 °C.

[0081] In samples No. 2 through 8, supports (or substrates) were arranged as shown in Fig.4 and then, vapor evaporation was conducted. Thus prepared radiation image conversion panel samples were each evaluated with respect to sharpness, luminance and luminance distribution, according to the following procedure.

## Evaluation of Sharpness

[0082] Modulation transfer function (MTF) was determined for each of the radiation image conversion panel samples to evaluate sharpness. Thus, after a CTF chart was adhered to the respective radiation image conversion panels, each of the panels was exposed at 10 mR of 80 kVp X-rays (at a distance to the object: 1.5 m). Thereafter, sample were each scanned with a semiconductor laser light beam (690 nm, a power of 40 mW on the panel) of 100  $\mu\text{m}$  diameter to read it. As shown in Table 1, MTF values (sharpness) of the respective panels were represented by the sum of the MTF values at 2.0 lp/mm.

## Evaluation of Luminance and Luminance Distribution

[0083] Samples were each evaluated with respect to luminance, using Regius 350, trade name, produced by Konica Corp. Thus, similarly to the foregoing sharpness evaluation, radiation image conversion panel samples were each exposed to X-rays of a tungsten bulb at 80 kVp and 10 mAs, at a distance between an X-ray source and the sample, and thereafter, the sample panel was set on the Regius 350 and read. Evaluation was made from electric signals obtained by a photomultiplier.

[0084] Distribution of electric signals within the exposed panel sample, obtained from the photomultiplier was eval-

uated. Thus, a standard deviation of the luminance distribution was determined for each panel sample (which was also denoted simply as S.D.). The less value indicates superior homogeneity of an activator.

Table 1

Sample No.	Activator	Substrate		Luminance	MTF (%)	S.D. (%)
		$\tau_g$	Angle ( $\theta_1 + \theta_2$ )			
1	Eu*	-	-	0.12	30	18
2	Eu	150	40°	1.82	31	10
3	Eu	200	40°	1.98	26	7
4	Eu	230	40°	2.01	33	8
5	Eu	300	40°	1.92	32	6
6	Eu	350	40°	2.11	33	4
7	Eu	280	40°	2.05	42	5
8	Eu	280	40°	2.11	40	7

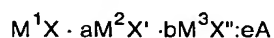
\*: Activator (Eu) was introduced in the wet process

[0085] As can be seen from Table 1, samples No. 2 through 8 were superior compared to sample No. 1.

## Claims

1. A radiation image conversion panel comprising on a support at least one stimuable phosphor layer comprising a stimuable phosphor, wherein the stimuable phosphor layer is a layer of vapor-deposited stimuable phosphor having a thickness of 50  $\mu\text{m}$  to 20 mm, and the support is comprised of a polymer material.
2. The radiation image conversion panel of claim 1, wherein the stimuable phosphor is represented by the following formula (1):

formula (1)



wherein  $M^1$  is at least one alkali metal atom selected from the group consisting of Li, Na, K, Rb and Cs;  $M^2$  is at least one divalent metal atom selected from the group consisting of Be, Mg, Ca, Sr, Ba, Zn, Cd, Cu and Ni;  $M^3$  is at least one trivalent metal atom selected from the group consisting of Sc, Y, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Al, Ga and In; X, X' and X'' are each a halogen atom selected from the group consisting of F, Cl, Br and I; A is a metal atom selected from the group consisting of Eu, Tb, In, Ce, Tm, Dy, Pr, Ho, Nd, Yb, Er, Gd, Lu, Sm, Y, Tl, Na, Ag, Cu and Mg; a, b and e are each  $0 \leq a < 0.5$ ,  $0 \leq b < 0.5$  and  $0 < e \leq 0.2$ .

3. The radiation image conversion panel of claim 2, wherein in the formula (1),  $M^1$  is at least one alkali metal atom selected from the group consisting of Rb and Cs.
4. The radiation image conversion panel of claim 1 or 2, wherein in the formula (1),  $M^2$  is at least one divalent metal atom selected from the group consisting of Be, Mg, Ca, Sr and Ba.
5. The radiation image conversion panel of claim 2, 3 or 4 wherein in the formula (1),  $M^3$  is at least one trivalent metal atom selected from Y, La, Ce, Sm, Eu, Gd, Al, Ga and In.
6. The radiation image conversion panel of claim 2, 3, 4 or 5, wherein in the formula (1), X is a halogen atom selected from the group consisting of F, Cl and Br.

7. The radiation image conversion panel of claim 1; 2, 3, 4, 5 or 6, wherein the stimuable phosphor is represented by the following formula (2):

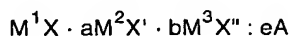
formula (2)



Wherein  $M^1$ , X, A and e are each the same as defined in formula (1).

8. The radiation image conversion panel of any of claims 1 to 7, wherein the polymer material exhibits a glass transition temperature of 150 to 350 °C.
9. The radiation image conversion panel of any of claims 1 to 8, wherein the polymer material is at least one selected from the group consisting of a cellulose acetate resin, polyester resin, polyethylene terephthalate resin, polyamide resin, epoxy resin, polyimide resin, triacetate resin, polycarbonate resin and syndiotactic polystyrene resin.
10. The radiation image conversion panel of any of claims 1 to 9, wherein the support is comprised of plural layers.
11. The radiation image conversion panel of claim 10, wherein the support is comprised of a polyimide layer, a carbon fiber plate layer and a polyimide layer in that order.
12. A method of preparing a radiation image conversion panel comprising on a support a stimuable phosphor layer, the method comprising:
- depositing a stimuable phosphor on the support by vapor deposition to form the stimuable phosphor layer, wherein the support is comprised of a polymer material.
13. The method of claim 12, wherein the stimuable phosphor layer has a thickness of 50 μm to 20 mm.
14. The method of claim 12, or 13, wherein the stimuable phosphor is represented by the following formula (1):

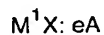
formula (1)



wherein  $M^1$  is at least one alkali metal atom selected from the group consisting of Li, Na, K, Rb and Cs;  $M^2$  is at least one divalent metal atom selected from the group consisting of Be, Mg, Ca, Sr, Ba, Zn, Cd, Cu and Ni;  $M^3$  is at least one trivalent metal atom selected from the group consisting of Sc, Y, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Al, Ga and In; X, X' and X'' are each a halogen atom selected from the group consisting of F, Cl, Br and I; A is a metal atom selected from the group consisting of Eu, Tb, In, Ce, Tm, Dy, Pr, Ho, Nd, Yb, Er, Gd, Lu, Sm, Y, Tl, Na, Ag, Cu and Mg; a, b and e are each  $0 \leq a < 0.5$ ,  $0 \leq b < 0.5$  and  $0 < e \leq 0.2$ .

15. The method of claim 12, 13 or 14, wherein the stimuable phosphor is represented by the following formula (2):

formula (2)



wherein  $M^1$ , X, A and e are each the same as defined in formula (1).

16. The method of claim 12, 13, 14 or 15, wherein the polymer material exhibits a glass transition temperature of 150 to 350 °C.

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17. The method of any of claims 12 to 16, wherein the polymer material is at least one selected from the group consisting of a cellulose acetate resin, polyester resins, polyethylene terephthalate resin, polyamide resin, epoxy resin, polyimide resin, triacetate resin, polycarbonate resin and syndiotactic polystyrene resin.

5 18. The radiation image conversion panel of claim 10 and the method of any of claims 12 to 17, wherein the support has a thickness of 80 to 2000  $\mu\text{m}$ .

19. The method of any of claims 12 to 18,  
wherein the support is comprised of plural layers.

10 20. The method of claim 19,  
wherein the support is comprised of a polyimide layer, a carbon fiber plate layer and a polyimide layer in that order.

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FIG. 1

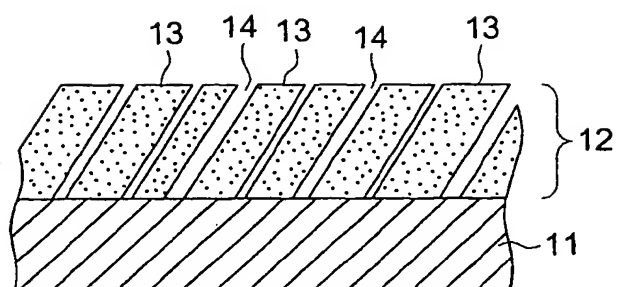


FIG. 2

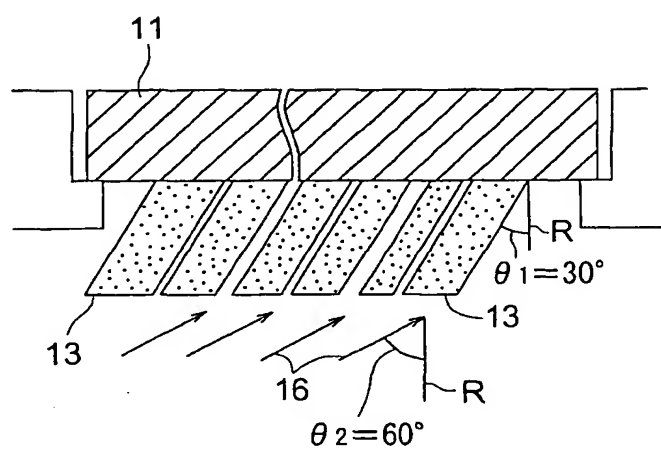


FIG. 3

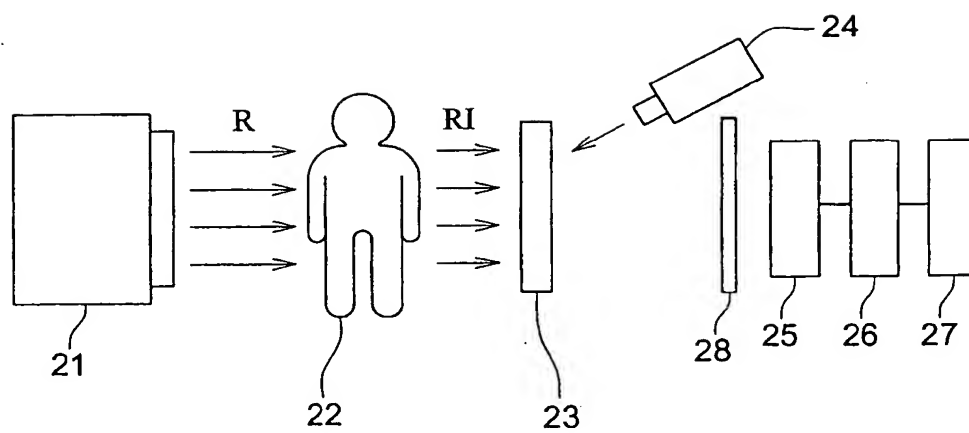
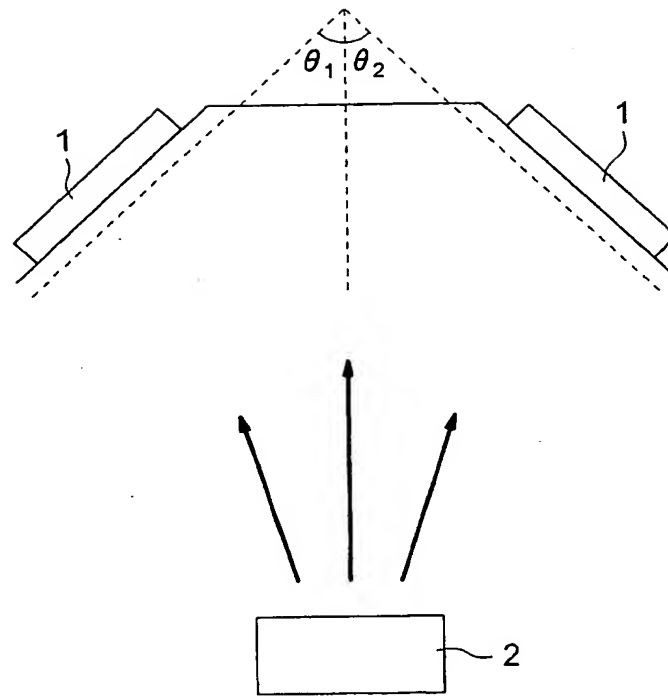


FIG. 4







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The present search report has been drawn up for all claims			
Place of search MUNICH		Date of completion of the search 15 September 2003	Examiner West, N
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons &amp; : member of the same patent family, corresponding document</p>			

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Place of search MUNICH		Date of completion of the search 15 September 2003	Examiner West, N
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